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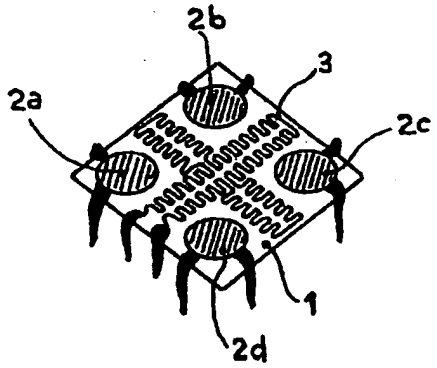

(57) Abstract

A device for sensing and measuring gaseous and/or vapor state analytes based on resonant piezoelectric layers, comprising a substrate from alumina (1), a plurality of sensors (2a, 2b, 2c, 2d) made from lead zirconate-titanate based piezoelectric elements, realized by means of a thick film technology on said substrate (1) and coated with sensitive coatings suitable to selectively and reversibly absorbing said analytes, at least a heating element (3) suitable to thermostate said substrate (1), as well as suitable circuits for the amplification, transmission and elaboration of the signals emitted by the sensors and suitable means for the treatment and electronic data processing and/or software.

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MULTI-SENSOR DEVICE FOR GRAVIMETRIC CHEMICAL MEASUREMENTS BY MEANS OF RESONANT PIEZOELECTRIC LAYERS BY THICK FILM TECHNOLOGY

DESCRIPTION

The present invention relates to a device for detecting, measuring and monitoring a plurality of gaseous and/or vapor state analytes, based on resonant piezoelectric elements, by means of a thick film technology.

As is known, the availability of chemical sensors having a good metrologic performance and low realization cost is required by many application situations. In particular, the detection of gaseous compounds and vapors in the air is an object of deep and topical interest for the environment monitoring, and for measurements in domestic and industrial environments.

The problem of chemical detection by means of electric output sensors is, as is well-known, a complex one, since it is extremely difficult to realize selective devices for the anlytes of interest, and it is substantially impossible to reach the response specificity.

Object of this invention is to provide a device for the detection, measurement and monitoring of gaseous and/or vapor state analytes different from one another and present at the same time in given environments, with high sensitivity and high selectivity and specificity.

Another objet of the invention is to provide a flexible, low cost multi-sensor device for gravimetric chemical measurements.

These and still other objects and related advantages which will be stressed by the following description, are achieved by a device for detecting and measuring gaseous and/or vapor state analytes, based on resonant piezoelectric layers, which device, according to the present invention, comprises:

- a substrate,
- a plurality of sensors made from piezoelectric elements based on compounds of polarized ferroelectric ceramics, realized by means of a thick film technology on said substrate and coated with sensitive coatings suitable to selectively and reversibly absorb said analytes,
- at least a heating element incorporated in said substrate, provided with a suitable regulation circuit apt to thermostate said substrate,

suitable circuits being also provided for the amplification, transmission and elaboration of the signals emitted by the sensors and suitable means for the treatment and electronic data processing and/or software.

More particularly, said substrate is made from alumina. The substrate may be also made from any other suitably insulated material, such as an enameled metal material, for instance enameled steel or the like.

Preferably, said compounds of ferroelectric ceramics are made from lead zirconate-titanate, and are realized by silk-screen printing on said substrate from alumina. As is known, the thick film technology allows to realize electronic devices and circuits by means of silk-screen printing processes of pastes having specific and different properties on suitable substrates, followed by thermal cycles to stabilize the mechanical and functional properties of the deposits.

The base material employed as an active phase for the preparation of the piezoelectric elements is lead zirconate-titanate of various compositions and particle sizes.

A binder is added to the powder lead zirconate-titanate, generally made from lead oxide (PbO) powder

or vitreous compounds, to promote the compacting of lead zirconate-titanate and its adhesion to the substrate during firing. The mixture made from lead zirconate-titanate and the binder is then dissolved in a liquid carrier made from an organic solvent and a thickener, typically ethyl cellulose in terpineol, to obtain a fluid compound having the right rheology to allow silk-screen printing.

After the printing, the layers are dried at about 150°C and then submitted to a firing process at about 950°C. After the firing, the piezoelectric activity is induced in the layers by means of a polarization process, namely the application of an electric field in the order of 4-5 MV/m for about 10 minutes, at a temperature near the Curie one (the typical values employed range from 100 to 200°C), followed by the return to ambient temperature with the applied field.

The piezoelectric and mechanical characteristics of the film depend on the composition of the paste and the mean particle size of the powders (typically comprised between 1 and 10 μm), the firing heat treatments, which concur as a whole to defining the microstructure of the layer and the polarization conditions.

The lead zirconate-titanate based resonant sensor on alumina substrate allows to detect small mass amounts integral with the vibrating structure through the decrease in the resonance frequency of the product, and can therefore advantageously detect a chemical species by means of the sensitization of the resonator with a material capable of reversibly absorbing the analyte of interest, with ensuing variation in its own mass.

The material that makes up said sensitive coatings that cover said piezoelectric elements and that are capable of reversibly absorbing the analyte of interest is generally a polymeric material, selected according to the analyte to be detected and measured.

It has been found that the substrate from alumina has an active role in the determination of the resonance frequency measured, which is not due to the piezoelectric layer only, but to the substrate/piezoelectric layer whole which constitutes therefore a composite resonator: in fact, it has been found that a reduction in the thickness of the substrate leads to an increase in resonance frequency and, correspondingly, in mass sensitivity. For a piezoelectric layer having a thickness of about 100 μm on a substrate of 250 μm, the frequency is of about 6,5

MHz and the sensitivity of -450 kHz/mg, which value is a remarkable result.

The device according to the invention is a gravimetric multi-sensor on one only substrate. Each microbalance of the whole is typically coated with a different sensitive material, so as to obtain for each analyte a range of different and complementary responses, to allow the detection through a suitable electronic processing and/or software.

The methods for processing response signals are complementary to the gravimetric multi-sensor system according to the present invention.

The parasitic influence of the operating temperature on the resonance frequency of the sensors according to the present invention is drastically reduced by means of a thermostating system. Such system employs a heating element silk-screen printed on the substrate, controlled by a regulation electronic circuit that keeps the temperature of the substrate at about 50°C, independently on ambient temperature. The electronic systems have been eliminated from the substrate which houses the sensors, as they are a disturbing heat source whose amount is not constant in time and which have not a uniform space distribution.

The temperature control system allows to markedly improve the stability of the resonance frequencies, the mass resolution and the minimum detectability threshold of the gaseous analytes of interest.

The invention will be described in the following with reference to the attached drawing, solely given by way of non limiting illustration of the invention, and wherein:

Figure 1 shows a device according to the present invention, comprising four resonant gravimetric sensors.

With reference to such figure, the device according to the invention comprises a substrate 1 from alumina of 2.5 x 2.5 cm. Four resonant piezoelectric layer sensors 2a, 2b, 2c and 2d from lead zirconate-titanate having a circular shape are present on substrate 1, near the corners of said substrate 1.

The piezoelectric element 2a is coated with poly(N-vinylpyrrolidone) and is sensitive to relative humidity; element 2b is coated with poly(amidoamine) and is sensitive to sulfur dioxide; element 2c is coated with polystyrene and is sensitive to aromatic hydrocarbons (e.g., toluene), while element 2d is

coated with poly(ethylenglicole) and is sensitive to aliphatic hydrocarbons (for instance, hexane).

On substrate 1, the meander-shaped, metal-based heating element 3 is also present in the central region of the substrate, according to a cross-geometry, to optimize symmetry.

The number of 4 sensors is merely indicative and, being not limited by any substantial constraint but the one of ensuring a symmetric arrangement of the sensors with respect to the heating elements, may be varied, in particular increased according to needs.

It must be taken into account that there unavoidably exists a tendency towards cross-sensitivity between the different sensors. In other words, sensor 2b of the example is sensitive to SO_2, but not only to it; in particular the sensitivity to SO_2 is appraisably affected, for instance, by the content of relative humidity of the environment (sensed by 2a).

This fact is due to the complexity of the chemical reactions involved in the analyte detection process which prevents an absolute response specificity. Being a multi-sensor device, the device according to the present invention provides an economical way to solve such problem as, to go back to the specific example,

one would not be able to tell, from the response of the individual sensor 2b, if said response is originated by SO_2, humidity or a mixture of the same. However, the response of 2a allows to determine the humidity content and therefore to separate from the signal of 2b only the contribution due to SO_2.

Through a suitable processing of the signals coming from the multiplicity of sensors, it is possible to exploit the information redundancy associated to non selective responses to obtain a reliable estimate of the composition of the atmosphere being examined. The higher the number of the sensors of the whole - insofar as allowed by the relative increase in the complexity of the system - the higher the detail by which said composition can be re-constructed.

Further advantages which the device according to the invention provides with respect to those of the known art - are in particular the following ones:

- the resonant piezoelectric layer sensing elements are planar, hence they need no additional and particular working steps;
- the realization of multi-sensor matrices is technically easy and economical;

- thermostating carefully all the matrix of the multi-sensor matrix is technically feasible and advantageous, as the thick film technology often allows to realize heating elements having widely variable geometries and sizes, and their localization on the same high thermal conductivity alumina substrate whereon sensors are placed maximizes the effectiveness of temperature regulation, keeping power consumption low;

- the system is miniaturized, compact, sturdy, without moving parts and has a low realization cost, even by reduced production volumes.

CLAIMS

1. A device for sensing and measuring gaseous and/or vapor state analytes based on resonant piezoelectric layers, which device, according to the present invention, comprises:

- a substrate (1);

- a plurality of sensors (2a, 2b, 2c, 2d) made from piezoelectric elements based on polarized ferroelectric ceramic compounds, realized with a thick film technology on said substrate (1), and coated with sensitive coatings suitable for selectively and reversibly absorbing said analytes;

- at least a heating element (3) incorporated in said substrate (1), provided with a suitable regulation circuit, suitable to thermostate said substrate (1), suitable circuits being also provided for the amplification, transmission and elaboration of the signals emitted by the sensors and opportune means for the treatment and electronic data processing and/or software.

2. The device according to claim 1, characterized in that said substrate (1) is made from alumina.

3. The device according to claim 1, characterized in that said substrate (1) is made from an insulated material, such as enameled steel.

4. The device according to claim 1, characterized in that said compounds of ferroelectric ceramics comprise lead zirconate-titanate.

5. The device according to claim 4, characterized in that said compounds of ferroelectric ceramics comprise, besides lead zirconate-titanate, binders such as lead oxide and/or vitreous compounds.

6. The device according to claims 1-5, characterized in that said piezoelectric elements made from lead zirconate-titanate are realized by silk-screen printing on said alumina substrate.

7. The device according to claim 1, characterized in that said heating element is silk-screen printed on said alumina substrate.

8. The device according to claim 1, characterized in that it is thermostated to 50°C by means of said heating element.

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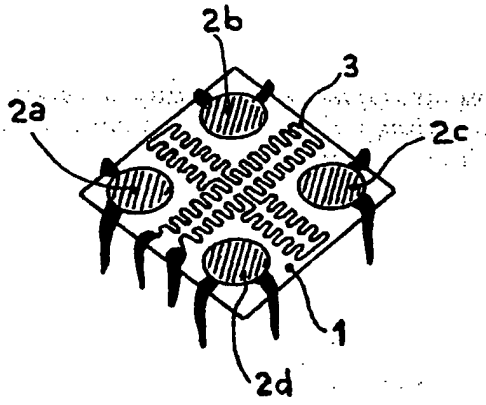

FIG.1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/06957

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N27/00 G01N33/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G01N G01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	V. FERRARI ET AL.: "Gravimetric chemical sensors in thick-film technology with hybrid electronics" CONFERENCE PROCEEDINGS. SAA '96 NATIONAL MEETING ON SENSORS FOR ADVANCED APPLICATIONS, BRESCIA, ITALY, 16-17 MAY 1996, vol. 54, 1997, pages 3-10, XP000865731 the whole document	1-8
Y	QU W ET AL: "DICKSCHICHT-GASSENSOREN IN INTEGRIERTER ANORDNUNG" TECHNISCHES MESSEN TM,DE,R.OLDENBOURG VERLAG. MUNCHEN, vol. 63, no. 11, November 1996 (1996-11), page 425-429 XP000679685 ISSN: 0171-8096 paragraphs '0001!,'0003!,'0005!; figure 2	1-8

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[X] Further documents are listed in the continuation of box C.

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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 719 441 A (HORN PETR) 12 January 1988 (1988-01-12) column 2, line 25-31	3
A	EP 0 603 945 A (ENIRICERCHE SPA ;SNAM SPA (IT)) 29 June 1994 (1994-06-29) abstract	6
A	ALTHAINZ P ET AL: "MULTISENSOR MICROSYSTEM FOR CONTAMINANTS IN AIR" SENSORS AND ACTUATORS B,CH,ELSEVIER SEQUOIA S.A., LAUSANNE, vol. B33, no. 1/03, 1996, page 72-76 XP000632926 ISSN: 0925-4005 abstract	1
A	MORTEN B ET AL: "A THICK-FILM RESONANT SENSOR FOR HUMIDITY MEASUREMENTS" SENSORS AND ACTUATORS A,CH,ELSEVIER SEQUOIA S.A., LAUSANNE, vol. A37-A38, June 1993 (1993-06), page 337-342 XP000411411 ISSN: 0924-4247 abstract	1

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information on patent family members

Intl. Appl. No. PCT/EP 99/06957

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4719441 A	12-01-1988	EP 0193015 A	03-09-1986
EP 0603945 A	29-06-1994	IT 1256759 B	15-12-1995
		AT 163092 T	15-02-1998
		DE 69316862 D	12-03-1998
		DE 69316862 T	03-09-1998
		ES 2113480 T	01-05-1998
		GR 3026284 T	30-06-1998
		JP 6229963 A	19-08-1994
		US 5400643 A	28-03-1995